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EFFECTIVE CROSS SECTION FOR PHOTOIONIZATION OF LITHIUM IONS

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The cross section for photoionization of the Li^+ ion in its ground state is calculated in the Coulomb interaction approximation. An approximate quantum-mechanical calculation of the Li^- photoionization cross section is carried out with allowance for a binding energy of $\epsilon = 0.80$ eV.

1. In spite of its simplicity, Li^+ cannot be regarded as a hydrogen-like ion because it has a filled shell $(1s)^2$. Therefore, the use of the exact formulas for photon absorption obtained from hydrogen functions is unjustified. For the same reason the method of calculating the photoionization coefficient of a valence electron, based on the use of the quantum defect and developed by Burgess and Seaton,[1] is in principle inapplicable to Li^+. Kramers's formula, obtained in the quasiclassical approximation, can give only a correct order of magnitude at low energies of the removed electron, and the probable error is not known.

A quantum-mechanical calculation of the cross section for photoionization of Li^+ in the ground state is given below on the assumption that the freed electron is subject only to the attractive Coulomb field of the residual ion.

The problem of the photoionization of Li^+ in the ground state is similar to photon absorption by H^-, since in both cases the initial electronic state is $(1s)^2$. In many papers dealing with the calculation of the atomic absorption coefficient of H^-, attention was concentrated on improving the accuracy of the initial-state wave function. Using a variational wave function, obtained in dealing with the energy eigenvalue problem, various authors successively increased the numbers of free parameters. Massey and Bates[2] solved the problem for three variational parameters; Williamson,[3] Henrich,[4] and Chandrasekhar[5] introduced wave functions with, respectively, five, ten, and eleven variational parameters. The results obtained by Henrich agree very well with those of Chandrasekhar and a further increase of the computational complexity is not justified because there is a considerable error due to representation of the matrix element of the transition in the form of a "dipole length" or "dipole velocity." In the present paper the photoionization of the Li^+ ion is dealt with using the currently most accurate wave function for the initial state.

The atomic absorption coefficient of Li^+ (in cm^2) for radiation of wavelength λ in the case when the removed electron moves at a velocity v along the direction z is given by

$$\sigma_\lambda = 6{,}812\cdot 10^{-20} k\,(k^2 + k_0^2)\,|\mu|^2;$$
$$\mu = \int \psi_d^* (z_1 + z_2)\,\psi_c\, d\mathbf{r}_1\, d\mathbf{r}_2, \tag{1.1}$$

where ψ_d is the normalized wave function of the initial state of the ion; ψ_c is the normalized wave function of the final state of the two electrons; z_1 and z_2 are the components of the radius-vectors of the two electrons in atomic units of length; k_0^2 is the ionization energy of the initial state expressed in rydbergs ($k_0^2 = 5.6$).

The wavelength λ (in angstroms) is related to the nondimensional electron momentum $k = \hbar v/e^2$ by

$$\lambda = 911.3/(k^2 + k_0^2). \tag{1.2}$$

As the wave function of the two-electron ground state of Li^+ we shall employ the ten-parameter expression of Chandrasekhar and Herzberg[6] who used a variational method:

$$\psi_d = Re^{-\alpha s}(1 + \beta u + \gamma t^2 + \delta s + \varepsilon s^2 + \zeta u^2 + \chi_6 su + \chi_7 t^2 u + \chi_8 u^2 + \chi_9 t^2 u^2), \tag{1.3}$$

where s, u, t are Hylleraas coordinates:

$$s = r_1 + r_2, \qquad t = r_2 - r_1, \qquad u = r_{12}.$$

The wave function of the final state of the two electrons, made symmetrical for both of them, has the form

$$\psi_c = \frac{1}{\sqrt{2}}\{\psi(r_1)\,\chi_{10}(r_2) + \psi(r_2)\,\chi_{10}(r_1)\}. \tag{1.4}$$

The exact wave function of the ground state of Li^{2+} is a hydrogen-like function of the form

$$\chi_{10}(r) = (Z^3/\pi)^{1/2} e^{-Zr}, \quad Z = 3. \tag{1.5}$$

As the wave function of the removed electron, $\psi(\mathbf{r})$, we shall use the wave function for an electron moving freely in the field of the Li^{2+} nucleus.

Massey and Bates [2] showed that in calculation of the atomic absorption coefficient the final-state wave function of Eq. (1.4) gives a sufficiently accurate result and the corrections representing higher approximations to ψ_c are not important. The effect of the polarization of the residual ion produced by the free electron field was neglected by Massey and Bates. Since the only electron of the Li^{2+} ion is in the K-shell, (1s), we can assume with sufficient accuracy that the free electron in the final state moves in the attractive Coulomb field of an effective charge $Z_1 = 2.7$. This value of Z agrees with Slater's rules [7] who recommended $Z_1 = Z - \Delta$ with $\Delta = 0.3$ for the residual 1s-electrons.

At infinity the wave function $\psi(\mathbf{r})$ should approach asymptotically a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and a converging spherical wave e^{ikr}/r. The required wave function has the form

$$\begin{aligned} \psi(r) &= N^{1/2} e^{i\mathbf{kr}} F(-iZ_1/k,\ 1,\ -i(kr + \mathbf{kr})), \\ N^{1/2} &= e^{\pi Z_1/2k} \,|\Gamma(1 + iZ_1/k)|, \end{aligned} \tag{1.6}$$

where F(a, b, c) is the confluent hypergeometric function.

The above wave function can be conveniently expanded in spherical functions:

$$\psi(r, \theta) = \sum_{l=0}^{\infty} R_l(r) P_l(\cos\theta). \tag{1.7}$$

The matrix element of the dipole transition contains only the p-wave and, therefore, the following expression is obtained for the radial wave function

$$\begin{aligned} R_1 &= re^{-ikr} f_1(r), \\ f_1(r) &= ike^{\pi Z_1/2k}\,|\Gamma(2 + iZ_1/k)|\, F(2 + iZ_1/k,\ 4,\ 2ikr). \end{aligned} \tag{1.8}$$

Calculation of the matrix element of the transition dipole moment using Eqs. (1), (3)—(8) gives the following result:

$$\begin{aligned} \mu = \frac{64\pi^2 RN}{3a^3} \Big\{ & \frac{24}{a^3}\Big(\beta + \frac{7\chi_6}{a} + \frac{56\chi_7}{a^2} \\ & + \frac{24\chi_8}{a^2}\Big[\frac{1}{ac^2} F\Big(d, 2, 4, \frac{2ik}{c}\Big) \\ & - \frac{1}{ab^2} F\Big(d, 2, 4, \frac{2ik}{b}\Big) - \frac{2}{b^3} F\Big(d, 3, 4, \frac{2ik}{b}\Big)\Big] \\ & + \frac{24}{a^4}\Big(\chi_6 - \frac{14}{a}\chi_7\Big)\Big[\frac{2}{c^3} F\Big(d, 3, 4, \frac{2ik}{c}\Big) \\ & + \frac{2}{b^3} F\Big(d, 3, 4, \frac{2ik}{b}\Big)\Big] + \chi_9 \frac{8!}{c^9} F\Big(d, 9, 4, \frac{2ik}{c}\Big) \\ & + \Big(\chi_7 + \chi_8 - \frac{6}{a}\chi_9\Big)\frac{7!}{c^8} F\Big(d, 8, 4, \frac{2ik}{c}\Big) \\ & + \Big(\gamma + \varepsilon + \zeta + \chi_6 - \frac{6}{a}\chi_7 + \frac{16}{a^2}\chi_9\Big)\frac{6!}{c^7} F\Big(d, 7, 4, \frac{2ik}{c}\Big) \\ & + \Big(\beta + \delta - \frac{6}{a}\gamma + \frac{6}{a}\varepsilon + \frac{3}{a}\chi_6 + \frac{12}{a^2}\chi_7 + \frac{12}{a^2}\chi_8 \\ & - \frac{40}{a^3}\chi_9\Big)\frac{5!}{c^6} F\Big(d, 6, 4, \frac{2ik}{c}\Big) \\ & + \Big(1 + \frac{3}{a}\delta + \frac{12\gamma + 12\varepsilon + 4\zeta}{a^2} + \frac{120}{a^4}\chi_9\Big) \\ & \times \frac{4!}{c^5} F\Big(d, 5, 4, \frac{2ik}{c}\Big) + \frac{24}{a^4}(\chi_7 - 3\chi_8) \\ & \times \frac{3!}{c^4} F\Big(d, 4, 4, \frac{2ik}{c}\Big) \\ & - \frac{12}{a^2}\Big(\beta + \frac{9\chi_6}{a} + \frac{30\chi_7}{a^2} + \frac{18\chi_8}{a^2}\Big)\frac{3!}{b^4} F\Big(d, 4, 4, \frac{2ik}{b}\Big) \\ & - \frac{2}{a}\Big(\beta + \frac{16\chi_6}{a} + \frac{20\chi_7}{a^2} + \frac{12\chi_8}{a^2}\Big)\frac{4!}{b^5} F\Big(d, 5, 4, \frac{2ik}{b}\Big) \\ & - \frac{8\chi_6}{a}\frac{5!}{b^6} F\Big(d, 6, 4, \frac{2ik}{b}\Big)\Big\}, \end{aligned}$$

$$a = Z + \alpha, \quad b = Z_1 + 2\alpha + ik,$$

$$c = \alpha + ik, \quad d = 2 + iZ_1/k,$$

$$N = ik^{1/2} Z_1^{1/2} Z^{3/2} \exp(\pi Z_1/2k)\,|\Gamma(2 + iZ_1/k)|. \tag{1.9}$$

Using Gauss's recurrence relations and the relationships between the hypergeometric and the elementary functions, we can reduce Eq. (19) to a form convenient for numerical computations. This form is very cumbersome and, therefore, it is not quoted here. Numerical calculations were carried out with an electronic computer "Ural-2" to an accuracy not exceeding 0.5%. The results are given in Fig. 1.

A similar calculation carried out using a wave function with only three variational parameters (α, β, and γ) gave too low a value of the photoionization cross section at the limit of the series: $\sigma = 0.486 \times 10^{-18}$ cm^2 instead of $\sigma = 1.44 \times 10^{-18}$ cm^2 which was found using the ten-parameter wave function. This indicates that the matrix element is sensitive to the wave function selected and

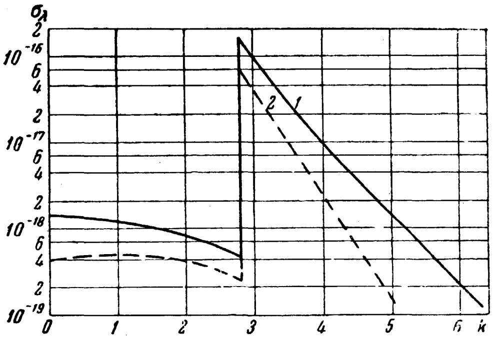

FIG. 1. Effective cross section for photoionization of the Li^+ ion as a function of the momentum of the removed electron; 1) calculated using an initial-state wave function with ten parameters [Eq. (1.3)]; 2) calculated using an initial-state wave function with three parameters (α, β, γ).

that it is necessary to use a large number of variational parameters. The unavoidable complexity of such calculations is justified because of the greater reliability of the final results.

The result obtained can be compared with an estimate of the photoionization cross section obtained using exact hydrogen functions:

$$\sigma = \frac{2^6 n^3 \pi}{Z_1^2} \left(\frac{\hbar c}{e^2}\right)^3 \sigma_0 \frac{1}{\gamma^4} F_n \left(\sqrt{\gamma - 1}\right) P_n \left(\frac{1}{\gamma}\right),$$

$$\sigma_0 = \frac{8\pi}{3} \left(\frac{e^2}{mc^2}\right)^2, \qquad \gamma = 1 + \frac{n^2}{Z_1^2} k^2. \tag{1.10}$$

Assuming as before that $Z_1 = 2.7$ and substituting $n = 1$ and $k = 0$, we obtain at the limit of the series a cross section $\sigma = 0.865 \times 10^{-18}$ cm^2. This demonstrates that the hydrogen-like approximation is not valid.

The approximate Kramers's formula with Gaunt's quantum-mechanical correction gives better agreement with the exact value: at the limit of the series $\sigma = 1.82 \times 10^{-18}$ cm^2. With increase of k the Kramers's cross section falls rapidly, i.e., this formula gives only a correct order of magnitude up to $k \approx 1$.

2. Cross sections for photon absorption by Li^- and H^- ions were obtained by Geltman[8] by an approximate method which allows for the interaction of a free electron with the residual atom by means of a truncated Coulomb potential. For H^- Geltman's method gave good agreement with the calculations of Henrich[4] and Chandrasekhar.[5] In calculation of the absorption by Li^- it was assumed that the wave function of the inner shell $(1s)^2$ is not affected and, therefore, this shell can be regarded as the "nucleus." Thus the numerical calculation in the case of Li^- is based on practically the same formulas as for H^- with the binding energy of the electron to the lithium atom taken as $\epsilon = 0.384$ eV. Recently new work has appeared[9-11] in which the electron affinity for the lithium atom is given as 0.74 eV $< \epsilon <$ 0.90 eV; Holøien[11] proposes $\epsilon = 0.81$ eV. In view of these new values we have used $\epsilon = 0.80$ eV.

The cross section for photoionization of Li^-, given in terms of the nondimensional electron momentum k, has the following form:[8]

$$\sigma_\lambda = \frac{32\pi^2}{3} \alpha a_0^2 \frac{k^2 + k_0^2}{k} \left| \int_0^\infty \varphi_0 \chi_1 r^2 dr \right|^2, \tag{2.1}$$

where α is the fine structure constant; a_0 is the Bohr orbit radius; $k_0^2 = 0.0591$ is the binding energy of the electron in rydbergs; φ_0 and χ_1 are the radial components of the wave function for a bound and free electron, respectively, found from Schrödinger's equation with the following truncated Coulomb potential:

$$V(r) = \begin{cases} 1/r_0 - 1/r, & r \leqslant r_0 \\ 0, & r \geqslant r_0. \end{cases} \tag{2.2}$$

The explicit form of the wave functions φ_0 and χ_1 is given in Geltman's work.[8] Using Moiseiwitsch's results,[10] it can be easily shown that for an electron binding energy $\epsilon = 0.80$ eV, the truncated Coulomb potential radius r_0 is 3.38. A numerical calculation of the photoionization cross section was carried out on a BÉSM electronic computer with an accuracy not greater than 2%. Figure 2 shows the calculated results for Li^- as a function of the nondimensional electron momentum. The relationship between the electron momentum k and wavelength is again given by Eq. (1.2).

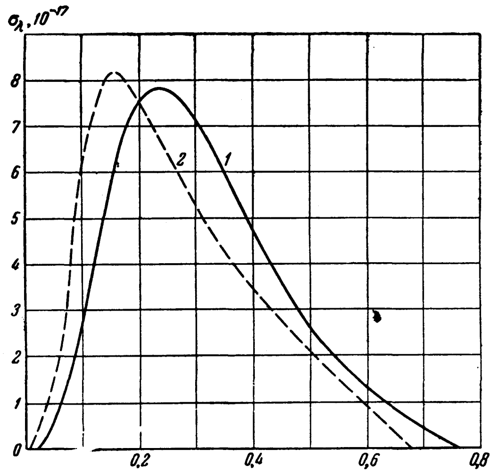

FIG. 2. Effective cross section for photoionization of the Li^- ion as a function of the momentum of the removed electron: 1) present author's result; 2) Geltman's curve.[8]

With an electron binding energy $\epsilon = 0.80$ eV the series limit $k = 0$ corresponds to $\lambda = 15410$ Å and consequently the maximum wavelength lies within the scope of a standard infrared spectrograph. Comparison of curves 1 and 2 in Fig. 2 shows that the dependence of the photoionization cross section for Li^+ on the electron momentum is not greatly affected by the value assumed for ϵ. It follows that the measured position of the emission maximum of Li^- in its continuous spectrum can be used to find the binding energy of an electron to a lithium atom.

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